

UDC 666.11.01:531.213.1:620.22

## CORRELATION BETWEEN ATOMIC STRUCTURE, STRUCTURAL NANOINHOMOGENEITY, AND QUADRATIC OPTICAL NONLINEARITY IN GLASSES OF THE $K_2O - TiO_2 - P_2O_5$ SYSTEM

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Translated from Steklo i Keramika, No. 1, pp. 7–11, January, 2006.

The methods of small angle synchrotron radiation scattering, vibration spectroscopy, and second harmonic generation are applied to glasses of the  $K_2O - TiO_2 - P_2O_5$  system near the stoichiometry of potassium titanyl-phosphate to demonstrate that at the initial stage of phase separation, while glass remains x-ray amorphous and clear, it can possess quadratic optical nonlinearity. The emergence of nonlinearity is facilitated by the formation of nanoheterogeneities in glass whose structure resembles the structural pattern of a nonlinear-optical crystal. A correlation established between the structural specifics of x-ray amorphous glass and its quadratic optical nonlinearity suggests the advisability of describing the short-range and medium-range orders of glasses at the glass-formation boundary in the context of quasicrystallite models.

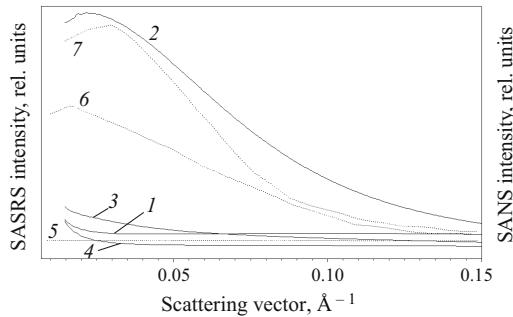
The needs of optoelectronic engineering has stimulated an increasing number of studies dedicated to new nonlinear-optic (NLO) materials, such as crystals, ceramics, clear glass ceramics, and lately glass as well. Glass is a centrosymmetric (CS) medium and, accordingly, does not have even-order optical nonlinearity. The transparency and stable properties of oxide glasses, the possibility of gradual variation of their properties and imparting virtually any shape to glass elements, and their low cost and technological availability attract the attention of researchers, who attempt to induce quadratic optical nonlinearity (QON) in glass [1–5].

One of the methods for inducing QON is homogeneous or heterogeneous nucleation of non-centro-symmetric crystals in a glass volume. It is possible to achieve the second optical harmonic generation (SHG) in such nano- or microstructured glasses while retaining the transparency of the medium. Due to a relatively low concentration and a random orientation of nanocrystals, the SHG signal is significantly weaker than in monocrystals of the same composition. Therefore, to produce nanostructured glasses with a high QON it is advisable, first, to select glass compositions and heat-treatment schedules ensuring the maximum formation of a NLO crystalline phase in glass and, second, to endeavor

to achieve the closest possible coordination between the refractive indexes of the matrix glass and crystals, which is especially important when crystals grow to submicron sizes, in which case media with QON comparable to that of monocrystals can be obtained. The possibility of significantly intensifying NLO effects by extruding nanostructural fiberglass and the prospects of the controlled development of complex surface and volumetric NLO structures separated by a clear matrix with a coordinated refractive index has generated even greater interest in glass as an active medium.

Both above specified conditions are frequently satisfied in homogeneous nucleation, where the initial glass has a composition similar to that of the crystalline phase emerging in this glass. Therefore, the  $K_2O - TiO_2 - P_2O_5$  system (KTP) can be regarded as a promising glass-forming system for nanostructured glasses in the composition range close to the stoichiometry of the ferroelectric potassium titanyl-phosphate crystal  $KTiOPO_4$ , which has exceptionally high QON. However, the composition  $K_2O \cdot 2TiO_2 \cdot P_2O_5$  is beyond the glass-formation range of the KTP system; therefore, a certain additional quantity of a glass-forming oxide has to be introduced into the batch to obtain such glasses. Thus, the authors of [4] used the sol-gel method to synthesize nanocomposite glass and glass ceramics of compositions  $(K_2O \cdot 2TiO_2 \cdot P_2O_5) - SiO_2$ , in which the SHG was registered. Glasses of the composition  $K_2O \cdot 2TiO_2 \cdot P_2O_5$  with additives  $SiO_2$ ,  $P_2O_5$ , and  $K_2O \cdot 2B_2O_3 \cdot 7SiO_2$  have been obtained [5–8] and their crystallization behavior and NLO

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**Fig. 1.** SANS and SASRS curves of initial and heat-treated glasses. SASRS: 1) KTP-10B initial; 2) KTP-10B-T heat-treated ( $580^{\circ}\text{C}$ , 30 min); 3) KTP-10Si; 4) KTP-7P; SANS: glasses KTP-10B: initial (5) and heat-treated at  $580^{\circ}\text{C}$  for 30 min (6) and 60 min (7).

properties, which depend significantly on the type of additive, have been studied. It was stated in [5, 6] that, depending on the additive type, the first crystalline nanophase may be either  $\text{KTiOPO}_4$ , or CS phases, which has a crucial effect on the formation of QON in clear glasses.

In order to identify the QON mechanisms at the early stages of phase separation, in the present study we investigated by means of Raman scattering (RS) and IR dielectric spectroscopy the structure of potassium-titanium-phosphate (PTP) glasses that have different crystallization properties and, consequently, different QON. To clarify the structural specifics of PTP glasses, we use a comparative analysis of vibration spectra of glasses obtained in our study and data on the spectra of the  $\text{KTiOPO}_4$  crystal [9 – 11].

For our study we selected glass compositions  $90(\text{K}_2\text{O} \cdot 2\text{TiO}_2 \cdot \text{P}_2\text{O}_5) \cdot 10\text{B}_2\text{O}_3$  (KTP-10B),  $90(\text{K}_2\text{O} \cdot 2\text{TiO}_2 \cdot \text{P}_2\text{O}_5) \cdot 10\text{SiO}_2$  (KTP-10Si), and  $93(\text{K}_2\text{O} \cdot 2\text{TiO}_2 \cdot \text{P}_2\text{O}_5) \cdot 7\text{P}_2\text{O}_5$  (KTP-7P) that have been studied by us previously [5, 6]. Glasses were prepared by fast cooling of melts; the melting and working procedure is described in detail in [5, 6]. The x-ray patterns of glasses were obtained using a DRON-3M diffractometer ( $\text{CuK}_\alpha$  radiation). The homogeneity of glasses under a nanoscale resolution was monitored using small angle synchrotron radiation scattering (SASRS) on the KWS-1 plant at the European Center for Synchrotron Radiation (Grenoble, France) with the scattering vector  $q = 4\pi\sin\Theta/\lambda$  varying from 0.15 to 0.25  $\text{\AA}^{-1}$ . Furthermore, for glasses  $90(\text{K}_2\text{O} \cdot 2\text{TiO}_2 \cdot \text{P}_2\text{O}_5) \cdot 10\text{B}_2\text{O}_3$  (KTP-10B) at various stages of heat treatment we obtained curves of small angle neutron scattering (SANS) within the range of  $q = 0.01 - 0.25 \text{\AA}^{-1}$  on a D11 diffractometer of the high-flux nuclear reactor at the Laut-Langeven Institute in Grenoble. Raman scattering (RS) spectra were registered in the frequency range of  $20 - 1700 \text{ cm}^{-1}$  using a T64000 triple spectrograph (Jobin Ivon); scattering was excited using the green line at 514.5 nm of a Stabilite 2017 Ar-laser (Spectra Physics). The dielectric spectra of the imaginary part of the electric permeability  $\epsilon''$  were obtained by combining mutually complementing measurements using the methods of precision monochromatic and reflective IR spectroscopy. We

measured complex transmission spectra in the frequency range of  $3 - 30 \text{ cm}^{-1}$  (an Epsilon submillimeter spectrometer) and reflections in the range of  $20 - 1000 \text{ cm}^{-1}$  (IR-Fourier-spectrometer “Bruker IFS-113v”). The obtained spectra were jointly processed using the dispersion analysis method. SHG measurements were performed at room temperature using a YAG:Nd laser ( $\lambda = 1064 \text{ nm}$ ). The standard reference sample was  $\alpha$ -quartz powder. All data on SCG signals are given in relative units  $I_{2\omega}/I_{2\omega}(\text{SiO}_2)$ , where  $I_{2\omega}$  is the intensity of SGG in the sample analyzed and  $I_{2\omega}(\text{SiO}_2)$  is the intensity of SHG in  $\alpha$ -quartz powder under the same parameters of the measuring device [5].

The x-rya phase analysis of initial PTP glasses and glass KTP-10B heat-treated at  $580^{\circ}\text{C}$  for 30 min (KTP-10B-T) demonstrated that neither initial glasses nor the heat-treated glass KTP-10B-T contain crystalline phases. Figure 1 shows the SASRS of initial PTP glass and glass KTP-10B: initial and heat-treated at  $580^{\circ}\text{C}$  for 30 and 60 min. The analysis of the SASRS and SANS curves suggests that the initial glasses KTP-7P and KTP-10B can be classified as homogeneous, i.e., not containing any phase heterogeneities, since the angle dependence  $I_{\text{SASRS}}(q)$  and  $I_{\text{SANS}}(q)$  for glass KTP-10B is absent. The calculation of the size of heterogeneities in the Guinier approximation indicated that glass KTP-10Si contains heterogeneities of size from 10 to 40  $\text{\AA}$ . Since the scattering intensity is not high, these heterogeneities can be characterized either by a small number or by a small difference between the electron density of the matrix and the particle. Electron microscopy data corroborate the absence of micro-heterogeneities in this glass [5]. Glass KTP-10B-T exhibits an extended nanostructure with the characteristic particle size equal to 45  $\text{\AA}$  according to SASRS and around 50  $\text{\AA}$  according to SANS data. The presence of a maximum in the SASRS curve suggests the existence of a well-correlated distance between the heterogeneities: approximately 300  $\text{\AA}$ . The size of heterogeneities in glass KTP-10B heat-treated twice as long (60 min) according to SANS data is around 65  $\text{\AA}$ .

Figure 2 shows the IR spectra of  $\epsilon''$  for PTP glasses. The spectra of glass KTP-10B are registered both for the initial glass and for glass heat-treated at  $580^{\circ}\text{C}$  for 30 min. The IR spectra of the initial and heat-treated glasses KTP-10B (i.e., the homogeneous and phase-separated glasses, according to SASRS and SANR data) virtually coincide. The main differences are insignificant variations in the relative intensities of some bands in the spectrum of glass after heat treatment. Thus,  $\epsilon''$  values in the maxima at frequencies about 475 and about  $620 \text{ cm}^{-1}$  are slightly higher and at frequencies about 712 and  $370 \text{ cm}^{-1}$  are slightly lower (in the latter case the frequency of the maximum decreased as well to  $360 \text{ cm}^{-1}$ ). The reason for the insignificant differences between the spectra of initial and heat-treated glass, in our opinion, is the fact that all atoms preserve their coordination numbers under heat treatment. Hence, it can be concluded that virtually all boron in the initial glass has a triangular coordination with respect to oxygen. This is evidenced by the intense (considering the low content of boron in glass) bands at 1200 and

1380 cm<sup>-1</sup>, which are not observed in other PTP glasses that do not contain boron. Since boron in glass is three-coordinated, it does not “draw” potassium atoms in constructing a mixed titanium-phosphate-borate lattice while passing to a four-coordination state, but constructs its own lattice consisting of BO<sub>3</sub> triangles. In fact, initial glass KTP-10B has the same atomic structure as phase-separated glass, and heterogeneous sites under heat treatment grow from 5–10 Å (not identifiable by SASRS and SANC methods) to about 50 Å in our case. A certain frequency shift and redistribution of band intensities can be attributed to the shift in the phase composition in the process of phase separation. A similar situation has been observed in other liquating glasses, for instance in sodium-silicate glasses [12].

The spectrum of glass KTP-10Si is similar to the spectra of glass KTP-10B. The analysis of published data suggests that some peculiarities of the spectrum  $\varepsilon''$  of glass KTP-10Si are related to Si–O vibrations, whereas the absence of these peculiarities in other spectra just corroborate their bond to silicon atoms. Thus, the band with a maximum at about 1000 cm<sup>-1</sup> is significantly more intense than in the spectrum of glass KTP-10B, which is presumably caused by the antisymmetric Si–O valence mode: the most intense band in the spectrum  $\varepsilon''$  of the vitreous SiO<sub>2</sub> (the antisymmetric valence mode of Si–O–Si bond) has a maximum at 1068 cm<sup>-1</sup> [11]. The wide intense peak at 350 cm<sup>-1</sup> perceptibly intensifies in the spectrum of glass KTP-10Si (370 and 360 cm<sup>-1</sup> in glass spectra KTP-10B and KTP-10B-T, respectively) and an arm emerges on the high-frequency slope of this peak at a frequency of about 440 cm<sup>-1</sup> (an arm is also present in glass spectra KTP-10B and KTP-10B-T, but at about 470 cm<sup>-1</sup>).

The intense peak in the range of 340–370 cm<sup>-1</sup> is present in all considered spectra  $\varepsilon''$  and, most probably, the main contribution to this spectrum is made by the vibration mode  $v_2$  of tetrahedrons PO<sub>4</sub>, whose frequency was calculated by Herzberg (1975) and found equal to 363 cm<sup>-1</sup>. This mode in the spectrum  $\varepsilon''$  of the single crystal KTiOPO<sub>4</sub> is represented by two peaks, which depending on the sample orientation are positioned at 364–385 and 400–404 cm<sup>-1</sup>, respectively [9]. In contrast, the arm at 440 cm<sup>-1</sup> is presumably a specific feature of the glass spectrum KTP-10Si and correlates with the deformation mode at 446 cm<sup>-1</sup> in the spectrum  $\varepsilon''$  of vitreous SiO<sub>2</sub> [11]. The spectrum KTP-10Si also has a weak band at 1150 cm<sup>-1</sup> which is absent in the spectra of other PTP glasses, whereas a band exists at 1164 cm<sup>-1</sup> in the spectrum  $\varepsilon''$  of quartz glass [11].

Thus, an assumption can be made regarding glass KTP-10Si, similarly to glass KTP-10B, that silicon does not modify the titanium-phosphate lattice, which remains close to the structural pattern of the KTiOPO<sub>4</sub> crystal, but constructs its own silicate structure. This hypothesis agrees with the nanophase heterogeneity of glass registered by the SASRS method and corroborates this model of the KTP-10Si glass structure proposed in our earlier studies [5, 7]. The low-frequency ranges of the spectra  $\varepsilon''$  of the considered

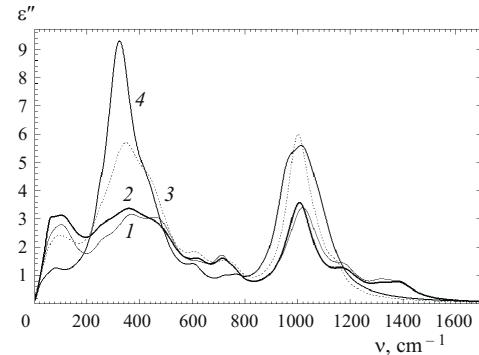


Fig. 2. IR spectra  $\varepsilon''$  of glasses KTP-10B (1), KTP-10B-T (2), KTP-10Si (3), and KTP-7P (4).

glasses have wide peaks at about 60 and about 100 cm<sup>-1</sup>. The spectra  $\varepsilon''$  of the crystal KTiOPO<sub>4</sub> in the range of 75–140 cm<sup>-1</sup> also have a large number of vibration resonances, which agrees with the hypothesis on the similarity of the short-range and medium-range structures of glasses KTP-10Si and KTP-10B to the structural patterns of crystalline KTiOPO<sub>4</sub>.

The IR spectrum  $\varepsilon''$  of glass KTP-7P differs significantly from the other spectra shown in Fig. 2. This difference consists in the absence of peaks related to silicate or borate additives, as well as in the difference from some spectra details common for glasses KTP-10Si and KTP-10B, which are presumably related to the structure of the KTP component. These differences are seen, for instance, in the ranges of 650–800 and 900–1100 cm<sup>-1</sup>; the wide intense peak at about 1000 cm<sup>-1</sup>, in contrast to other spectra, evidently consists of two highly overlapping peaks. Note that the low-frequency spectrum range (<150 cm<sup>-1</sup>) of glass KTP-7P also differs perceptibly from the spectra of other PTP glasses, which is manifested in a shift of the maximum frequency and in significantly lower intensity. This is possibly due to the fact that glass KTP-7P is the only homogeneous glass whose composition is outside the liquation range. Unlike the three other glasses, this glass under heat treatment generates the CS phase KTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> [8], which, considering the similarity of the compositions of initial glass and the crystals, can be reasonably attributed to a homogenous crystallization of glass without preceding amorphous phase separation.

Figure 3 shows the RS specters of the considered glasses, as well as the RS spectrum of crystalline KTiOPO<sub>4</sub> based on Kugel's data [9]. The RS spectra of glasses KTP-10B and KTP-10B-T also corroborate the proposed structural model of glass KTP-10B, since they are very close for the initial and heat-treated glasses. The difference consists only in the fact that the spectrum of the heat-treated glass shows ordering of the PTP phase, which approaches the structure of KTiOPO<sub>4</sub>. The RS spectrum of heat-treated glass KTP-10B-T has some peaks common with the initial glass, as well as new peaks at 560 and 620 cm<sup>-1</sup>, which have analogs in the spectrum of KTiOPO<sub>4</sub>. The boson peak becomes sharper, and its maximum frequency (about 80 cm<sup>-1</sup>)

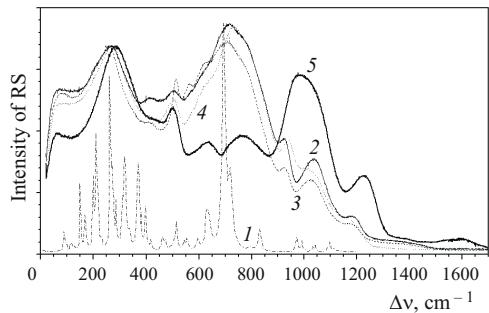


Fig. 3. RS spectra of KTiOPO<sub>4</sub> crystal (1) and glasses KTP-10B (2), KTP-10B-T (3), KTP-10Si (4), and KTP-7P (5).

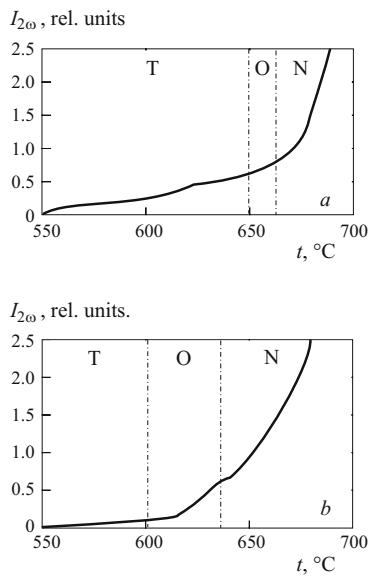


Fig. 4. Dependence of the SHG signal on temperature under 1 h heat treatment for glasses KTP-10Si (a) and KTP-10B (b): T) transparent glasses; O) opalescent; N) non-transparent.

is nearer to the frequency of the band at 90  $\text{cm}^{-1}$  in the crystal spectrum, compared to the boson peak in the initial glass.

The RS spectra of glasses KTP-10B and KTP-10Si are close and the peaks of these spectra correlate mainly with bands or groups of bands in the spectrum of the KTiOPO<sub>4</sub> crystal. Thus, the most intense band in the spectra of these glasses with a maximum around 715  $\text{cm}^{-1}$  for KTP-10B and 730  $\text{cm}^{-1}$  for KTP-10Si correlates with the most intense band at 700  $\text{cm}^{-1}$  corresponding to the vibration  $\nu_1$  of TiO<sub>6</sub> octahedrons in the KTiOPO<sub>4</sub> crystal [9]. A wide intense band with a maximum around 270  $\text{cm}^{-1}$  corresponds to a series of bands in the crystal spectrum within the frequency interval of 200–400  $\text{cm}^{-1}$  related mainly to the vibrations of K–O links and various vibration modes of TiO<sub>6</sub> octahedrons [9]. The band around 930  $\text{cm}^{-1}$  and the arm around 770  $\text{cm}^{-1}$  in the glass spectra have no obvious analogs in the KTiOPO<sub>4</sub> structure, but according to the data in [10], intense bands arise at 920 and 770  $\text{cm}^{-1}$  in the spectrum of the KTiOPO<sub>4</sub> melt, presumably corresponding to the vibrations of PO<sub>4</sub> tet-

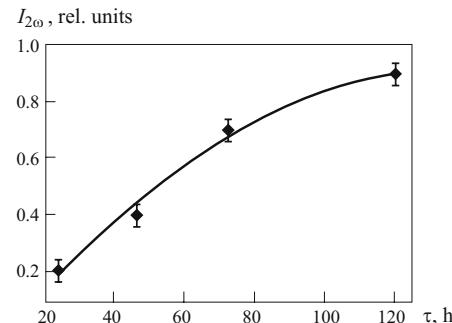
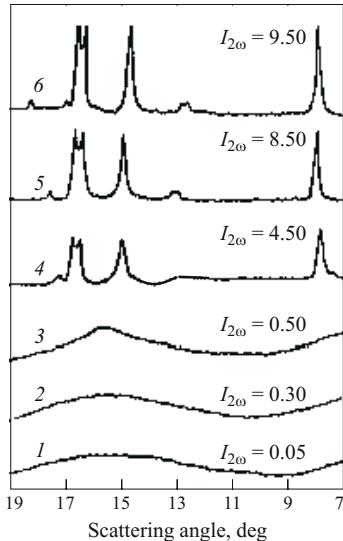


Fig. 5. Dependence of SHG signal on heat treatment duration at 640°C for glass KTP-10Si.

rahedrons and titanium-oxygen complexes in the melt. The low-frequency range of the glass spectra has boson peaks at a frequency of about 74  $\text{cm}^{-1}$ , whereas the low-frequency spectrum of KTiOPO<sub>4</sub> is represented by a relatively intense band at 90  $\text{cm}^{-1}$  and a series of weak bands in its vicinity. Thus, it is logical to assume that both short-range and medium-range orders of glasses KTP-10B and KTP-10Si are similar to each other and to the structural pattern of the KTiOPO<sub>4</sub> crystal.

The RS spectrum of glass KTP-7P, in contrast to those considered above, does not suggest analogies with the spectrum of the KTiOPO<sub>4</sub> crystal. Based on the data in [9, 13], it can be assumed that the spectrum bands of glass KTP-7P with maxima around 500, 980, and 1230  $\text{cm}^{-1}$  are related to various vibrations of P–O complexes. A boson peak with the maximum frequency of 58  $\text{cm}^{-1}$  is observed in the low-frequency range, which also differs perceptibly from the frequency of the main low-frequency band in the KTiOPO<sub>4</sub> spectrum (90  $\text{cm}^{-1}$ ). Thus, the short- and medium-range orders of glass KTP-7P are constructed in accordance with a certain phase different from KTiOPO<sub>4</sub>, most probably the CS phase KTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, which is the first to crystallize from this glass [9] and to which the glass composition is shifted from the stoichiometry of KTiOPO<sub>4</sub>.

In our previous studies [5, 8] we published data on SHG signals from glass KTP-10Si shown in Figs. 4 and 5. Figure 4a shows the dependence of the SHG signal of glass KTP-10Si on heat treatment temperature [8]. The glass retains its clarity at temperatures up to 650°C. Note that this boundary is near the vitrification temperature for this glass (634°C) [7]. Figure 5 shows the dependence of the SHG signal on the duration of heat treatment near the clarity range boundary [5]. It can be seen that the intensity of SHG grows with increasing heat treatment duration, while the glass retains its clarity. Figure 6 shows the x-ray patterns of the initial glass KTP-10Si and glass samples KTP-10Si heat-treated at various temperatures, as well as the respective values of the SHG signals obtained from these samples. The diffraction patterns of glasses heat-treated at 727°C or higher have sharp peaks indicating the emergence of a crystalline structure; furthermore, the positions of these peaks correlated with the diffraction pattern of crystalline KTiOPO<sub>4</sub>. How-



**Fig. 6.** X-ray patterns and SHG signal (relative units) of transparent (1, 2), opalescent (3), and opaque (4–6) samples of glass KTP-10Si: 1) initial; 2) 427°C, 1 h; 3) 627°C, 2 h; 4) 727°C, 1 h; 5) 800°C, 1 h; 6) 627°C, 2 h + 800°C, 1 h.

ever, a SCG signal, although a less intense one, has been also obtained from glasses heat-treated at temperatures below 650°C, which are x-ray-amorphous, and even from the initial glass, which agrees with the SASRS on the presence of nanoheterogeneities in the initial glass.

The dependence of the SHG signal of glass KTP-10B on heat treatment temperature is shown in Fig. 4b. Qualitatively, it is similar to such dependence for glass KTP-10Si, and only the boundary temperatures of clarity, opalescence, and opacity zones differ. For glass KTP-10B the clarity zone boundary is 600°C, which, as in the case of glass KTP-10Si, is near its vitrification temperature (585°C). The SHG signal in a sample studied by the vibration spectrometry method was equal to 0.05 quartz reference standard. Glasses KTP-7P, whether initial or heat treated according to various schedules, have no SHG.

It is logical to assume that the formation of QON in glasses KTP-10B and KTP-10Si under heat treatment is related to the similarity of the short-and medium-range orders of glasses KTP-10B and KTP-10Si to each other and to the structural pattern of the  $\text{KTiOPO}_4$  crystal. In contrast to that, glass KTP-7P has no QON, either in the homogeneous or in the phase-separated state, which agrees with its assumed structural similarity to the CS phase  $\text{KTi}_2(\text{PO}_4)_3$  which crystallizes in this glass.

Thus, the present study for the first time established a correlation between the atomic structure of initial glass, its phase separation and crystallization, and QON arising in glass in this case. The correlation observed between the structural specifics of x-ray-amorphous glasses and their QON suggests the advisability of describing the short-range and medium-range orders of glasses, whose compositions are near glass-formation boundaries, in the context of quasi-crystallite models. It follows from the obtained results that at

the stage of amorphous phase separation, when the glass is characterized by fully diffuse x-ray scattering, it can have or not have QON depending on its medium-range scale structure. The formation of QON makes the short- and medium-range orders of glass closer to the structural pattern of a NLO crystal. An increase in the size of polar heterogeneities perceptibly increases the efficiency of SHG. Understanding the correlation between the specifics of glass structure and its quadratic optical nonlinearity is a necessary condition for advances in the technology of nonlinear-optical materials required in optics, optoelectronics, and telecommunications.

*The study was performed with the financial support of the Russian Foundation for Basic Research (grants 04-03-3254 and 03-02-16720) and NATO program "Science for Peace" (grant 977980).*

## REFERENCES

1. R. A. Myers, N. Mukherjee, and S. R. J. Brueck, "Large second-order nonlinearity in poled fused silica," *Opt. Lett.*, **16**(22), 1732 – 1734 (1991).
2. M. Abe, T. Kitagawa, K. Hattori, et al., "Electrooptical switch constructed with a poled silica-based waveguide on a Si substrate," *Electron. Lett.*, **32**(10), 893 – 894 (1996).
3. N. Tamagawa, Y. Benino, T. Fujiwara, and T. Komatsu, "Thermal poling of transparent  $\text{TeO}_2$ -based nanocrystallized glasses and enhanced second harmonic generation," *Opt. Commun.*, **217**, 387 – 394 (2003).
4. Donglin Li, Lingbin Kong, Liangying Zhang, and Xi Yao, "Sol-gel preparation and characterization of transparent  $\text{KTiOPO}_4/\text{SiO}_2$  nanocomposite glass for second harmonic generation," *J. Non-Cryst. Solids*, **271**, 45 – 55 (2000).
5. V. N. Sigaev, Pernice, A. Aronne, et al., "KTiOPO<sub>4</sub> precipitation from potassium titanium phosphate glasses, producing second harmonic generation," *J. Non-Cryst. Solids*, **292**, 59 – 69 (2001).
6. A. Aronne, L. E. Depero, V. N. Sigaev, et al., "Structure and crystallization of potassium titanium phosphate glasses containing  $\text{B}_2\text{O}_3$  and  $\text{SiO}_2$ ," *J. Non-Cryst. Solids*, **324**, 208 – 219 (2003).
7. V. N. Sigaev, Pernice, L. E. Depero, et al., "Nanostructuring in potassium titanium phosphate glasses containing  $\text{SiO}_2$ ," *J. Europ. Ceram. Soc.*, **24**(6), 1949 – 1952 (2004).
8. V. N. Sigaev, Pernice, A. Aronne, et al., "Nano-Phased crystallisation of ferroelectrics from glasses in the  $\text{K}_2\text{O} - \text{TiO}_2 - \text{P}_2\text{O}_5$  and  $\text{K}_2\text{O} - \text{Nb}_2\text{O}_5 - \text{SiO}_2$  systems," *Integr. Ferroelectrics*, **61**, 249 – 253 (2004).
9. G. E. Kugel, F. Bréhat, B. Wyncke, et al., "The vibrational spectrum of a  $\text{KTiOPO}_4$  single crystal studied by raman and infrared reflectivity spectroscopy," *J. Physics C: Solid State Phys.*, **21**, 5565 – 5583 (1988).
10. Yu. K. Voron'ko, V. A. D'yakov, A. B. Kudryavtsev, et al., "A study of phase transformations in  $\text{KTiOPO}_4$  using the Raman scattering method," *Fiz. Tverd. Tela*, **31**(10), 150 – 156 (1989).
11. M. K. Gunde, "Vibrational modes in amorphous silicon dioxide," *Physica B*, **292**, 286 – 295 (2000).
12. S. Fujita, Y. Kato, and M. Tomozawa, "IR peak shift due to phase separation of  $\text{Na}_2\text{O} - \text{SiO}_2$  system glasses," *J. Non-Cryst. Solids*, **328**, 64 – 70 (2003).
13. R. K. Brow, "Review: the structure of simple phosphate glasses," *J. Non-Cryst. Solids*, **263&264**, 1 – 28 (2000).